aqueous solutions of potassium ferrocyanide separated by a membrane of colloidal copper ferrocyanide is given by the equation—

$$\pi_2 - \pi_1 = \frac{RT}{F} \log \frac{a_1}{a_2}, \qquad \text{(ii)}$$

where a_1 and a_2 are the "activities" of the potassium ion in the two solutions. It will be observed that equation (ii) reduces to equation (i) when the concentrations of the potassium ions are proportional to their activities.

Morphological Studies of Benzene Derivatives. VI.—*Para-sulphonic Derivatives of Chloro-, Bromo-, Iodo-, and Cyanobenzene.*

By C. S. Mummery, B.Sc.

(Communicated by Prof. H. E. Armstrong, F.R.S. Received May 28,—
Read June 25, 1914.)

The compounds described in this communication were examined in order to contrast the para-mono-derivatives of benzenesulphonic acid with the di-derivatives studied by Colgate and Rodd.* It is unnecessary to describe the methods used in preparing them, as these are well known.

The melting points of the various compounds are given in the following Table :—

1	4				
	SO_2Cl	SO_2Br	$SO_2.NH_2$	$SO_2NH.Ph$	$SO_2NH.C_6H_4.CH_3$
Cl	53·5°	56°	143·5°	104°	87°
Br	74·5	77	165	118	94
I	84	97	190	143	129
CN	109	—	167	—	—

It is noticeable that the substitution of one halogen for another in the sulphonic radicle makes but a small difference in the melting point (about 3°) in comparison with that produced (about 20°) by a similar substitution in the nucleus.

In the case of the sulphochlorides and of the sulphonamides, the crystallographic constants of similar compounds containing different halogens are practically identical:—

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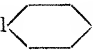
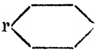
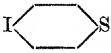
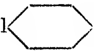
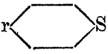
* These Studies.—Part II, 'Chem. Soc. Trans.,' 1910, p. 1585.

Compound	Axial ratios $a : b : c$	β
ClSO_2Cl..............	0·840 : 1 : 2·079	83° 31′
BrSO_2Cl..............	0·820 : 1 : 2·074	83 13
ISO_2Cl..............	0·839 : 1 : 2·074	84 38
ClSO_2NH_2...........	0·629 : 1 : 0·603	82 12
BrSO_2NH_2...........	0·628 : 1 : 0·601	81 4

Parachlorobenzenesulphochloride, $C_6H_4Cl.SO_2Cl$.—This compound was obtained in measurable crystals from a mixture of benzene and light petroleum. Some difficulty was experienced in producing crystals which had sufficient forms for calculation.

System: Monosymmetric.

Axial ratios: $a : b : c = 0{\cdot}840 : 1 : 2{\cdot}079$. $\beta = 83° 31′$.

Forms observed: {001}, {101}, {10$\bar{1}$}, {011}.

Angle	No. of observations	Limits	Mean	Calculated
001 : 10$\bar{1}$	27	116° 52′—117° 51′	117° 29′	—
101 : 10$\bar{1}$	22	43 31 — 44 8	43 49	—
001 : 011	41	63 42 — 64 39	64 11	—
001 : $\bar{1}$01	29	62 6 — 63 0	62 26	62° 30′
011 : 01$\bar{1}$	31	51 6 — 51 49	51 32	51 37
011 : $\bar{1}$01	33	77 51 — 78 53	78 19	78 24
011 : 10$\bar{1}$	32	101 20 —101 58	101 40	101 36

Several crystals of a labile modification were also deposited, but sufficient measurements for the calculation of their constants were not obtained.

Parachlorobenzenesulphobromide, $C_6H_4Cl.SO_2Br$.—Considerable difficulty was experienced in crystallising this substance in measurable form: it was eventually obtained from a mixture of benzene and light petroleum.

System: Monosymmetric.
Axial ratios: $a : b : c = 1{\cdot}901 : 1 : 1{\cdot}527$. $\beta = 88° 26'$.
Forms observed: $\{100\}$, $\{101\}$, $\{\bar{1}01\}$, $\{110\}$.

Angle	No. of observations	Limits	Mean	Calculated
$100 : \bar{1}01$	15	129° 21′—130° 11′	129° 43′	—
$100 : 110$	36	61 47 — 62 35	62 14	—
$100 : 101$	9	51 57 — 52 31	52 11	—
$101 : 110$	13	72 21 — 72 56	72 37	72° 41′
$110 : \bar{1}10$	21	55 13 — 55 59	55 34	55 32
$101 : \bar{1}01$	6	77 14 — 77 57	77 30	77 32
$\bar{1}01 : \bar{1}00$	23	49 59 — 50 41	50 20	50 17
$110 : \bar{1}01$	13	107 1 —107 41	107 21	107 19

Several crystals of a labile modification were also deposited but sufficient measurements for the calculation of their constants were not obtained.

Parachlorobenzenesulphonamide, $C_6H_4Cl.SO_2.NH_2$. — Measurable crystals were deposited from a solution in acetone; crystals of one crop gave an electric discharge from opposite ends of an axis.

System: Monosymmetric.
Axial ratios: $a : b : c = 0{\cdot}629 : 1 : 0{\cdot}603$. $\beta = 82° 12'$.
Forms observed: $\{100\}$, $\{010\}$, $\{121\}$, $\{012\}$, $\{210\}$, $\{\bar{1}11\}$.

Angle	No. of observations	Limits	Mean	Calculated
$010 : 210$	22	72° 14′—73° 10′	72° 38′	—
$010 : 012$	19	73 1 —73 49	73 23	—
$012 : \bar{1}00$	11	82 15 —82 57	82 32	—
$010 : \bar{1}11$	23	67 5 —67 59	67 39	67° 35′
$\bar{1}11 : \bar{1}\bar{1}1$	9	44 27 —45 19	44 48	44 50
$210 : 2\bar{1}0$	11	34 16 —35 4	34 48	34 44
$012 : 0\bar{1}2$	9	32 57 —33 59	33 27	33 14
$100 : 012$	11	97 4 —97 57	97 26	97 28
$210 : 100$	11	16 40 —17 45	17 19	17 22
$010 : 121$	21	46 30 —47 36	47 4	47 9
$121 : 1\bar{2}1$	12	85 55 —86 29	86 3	85 43

The corresponding anilide was obtained but not in measurable crystals; it closely resembles the corresponding bromanilide.

Parachlorobenzenesulphoparatoluidide, $C_6H_4Cl\ SO_2.NH.C_6H_4.CH_3$.—Measureable crystals were obtained from a solution in ethylic acetate.

System: Anorthic.
Axial ratios: $a : b : c = 1{\cdot}020 : 1 : 1{\cdot}096$.
$\alpha = 106° 6'$. $\beta = 93° 50'$. $\gamma = 77° 29'$.
Forms observed: $\{100\}$, $\{001\}$, $\{010\}$, $\{101\}$, $\{10\bar{1}\}$, $\{11\bar{1}\}$, $\{01\bar{1}\}$.

Angle	No. of observations	Limits	Mean	Calculated
100 : 010	26	74° 0′— 74° 46′	74° 21′	—
010 : 00$\bar{1}$	21	101 36 —102 19	101 56	—
001 : 01$\bar{1}$	18	55 7 — 55 47	55 31	—
100 : 00$\bar{1}$	17	89 20 — 89 49	89 36	—
100 : 10$\bar{1}$	17	42 0 — 42 43	42 19	—
100 : 01$\bar{1}$	9	76 16 — 76 48	76 30	76° 33′
010 : 10$\bar{1}$	9	86 17 — 86 48	86 27	86 31
011 : 010	16	46 2 — 46 43	46 25	46 25
010 : 001	17	77 47 — 78 24	77 58	78 4
010 : $\bar{1}$00	25	105 13 —105 59	105 39	105 39
100 : 11$\bar{1}$	12	43 4 — 43 36	43 18	43 4
01$\bar{1}$: $\bar{1}$00	8	103 12 —103 27	103 20	103 27
11$\bar{1}$: 01$\bar{1}$	8	33 16 — 33 35	33 23	33 29
010 : 11$\bar{1}$	6	49 53 — 50 21	50 5	50 24
11$\bar{1}$: 10$\bar{1}$	5	35 41 — 36 36	36 7	36 7
10$\bar{1}$: 0$\bar{1}$0	5	93 1 — 94 6	93 34	93 29
100 : 001	17	90 9 — 90 57	90 21	90 24
10$\bar{1}$: 00$\bar{1}$	16	46 59 — 47 41	47 17	47 17
100 : 101	9	42 25 — 43 17	42 51	—
101 : 001	6	47 16 — 47 50	47 34	—

Parabromobenzenesulphochloride, $C_6H_4Br.SO_2Cl$.—Measurable crystals were obtained from a mixture of benzene and light petroleum.

System: Monosymmetric.

Axial ratios: $a : b : c = 0{\cdot}820 : 1 : 2{\cdot}074$. $\beta = 83' 13'$.

Forms observed: {001}, {10$\bar{1}$}, {011}, {012}.

Angle	No. of observations	Limits	Mean	Calculated
101 : 10$\bar{1}$	12	42° 27′— 43° 12′	42° 57′	—
10$\bar{1}$: 001	24	116 44 —117 36	117 21	—
001 : 011	41	63 40 — 64 28	64 6	—
001 : $\bar{1}$01	21	62 32 — 63 15	62 47	62° 39′
011 : $\bar{1}$01	33	77 52 — 78 54	78 34	78 27
011 : 10$\bar{1}$	36	101 1 —101 56	101 28	101 33
011 : 01$\bar{1}$	19	51 24 — 52 11	51 42	51 48
011 : 012	5	17 53 — 18 5	18 0	18 17
012 : 001	7	45 23 — 46 14	45 58	45 49

The corresponding bromide was not obtained in measurable form.

Parabromobenzenesulphonamide, $C_6H_4Br.SO_2.NH_2$.—This amide was obtained in measurable form from a solution in acetone.

System: Monosymmetric.

Axial ratios: $a : b : c = 0{\cdot}628 : 1 : 0{\cdot}601$. $\beta = 81° 4'$.

Forms observed: {100}, {101}, {210}, {111}, {121}, {012}, {$\bar{1}$11}.

Angle	No. of observations	Limits	Mean	Calculated
$010 : 210$	46	72° 12′—73° 16′	72 46	—
$010 : 012$	36	73 4—73 53	73 27	—
$012 : \bar{1}00$	12	81 6—81 48	81 26	—
$012 : 0\bar{1}2$	20	32 44—33 31	33 6	33° 6′
$210 : 100$	26	16 43—17 46	17 13	17 14
$100 : 012$	11	98 12—98 59	98 34	98 34
$210 : 2\bar{1}0$	13	34 5—34 51	34 30	34 26
$010 : 121$	65	46 3—47 25	46 50	46 57
$121 : 1\bar{2}1$	32	85 52—86 54	86 14	86 6
$010 : \bar{1}11$	45	67 49—68 49	68 11	68 13
$\bar{1}11 : \bar{1}\bar{1}1$	21	43 1—43 54	43 38	43 34
$111 : 121$	2	17 56—18 1	17 58	18 1
$111 : 101$	2	24 32—25 2	24 47	25 2
$121 : 101$	2	42 59—43 30	43 14	43 3

An electric discharge from opposite ends of an axis was obtained from crystals of several crops of this substance.

Parabromobenzenesulphanilide, $C_6H_4Br.SO_2.NH.C_6H_5$.—This substance forms hemimorphic, orthorhombic crystals of very peculiar habit: the measurements are therefore withheld until it has been submitted to further study.

The corresponding paratoluidide appears to resemble the corresponding chloro-derivative very closely.

Pariodobenzenesulphonic chloride, $C_6H_4I.SO_2Cl$.—This chloride was deposited in measurable crystals from a mixture of benzene and light petroleum.

System : Monosymmetric.

Axial ratios: $a : b : c = 0{\cdot}839 : 1 : 2{\cdot}074$. $\beta = 84° 38'$.

Forms observed: $\{001\}, \{10\bar{1}\}, \{111\}, \{011\}, \{012\}$.

Angle	No. of observations	Limits	Mean	Calculated
$001 : 011$	28	63° 43′— 64° 37′	64° 8′	—
$011 : 10\bar{1}$	21	101 5—101 55	101 16	—
$10\bar{1} : 111$	14	55 29— 56 18	55 49	—
$011 : \bar{1}01$	22	78 35— 78 57	78 44	78° 44′
$011 : 012$	7	18 2— 18 21	18 9	18 4
$012 : 001$	7	45 39— 46 4	45 53	45 54
$001 : 10\bar{1}$	13	116 22—116 46	116 28	116 36

The bromide, amide, anilide, and paratoluidide of the iodo-acid were also prepared, but not obtained in measurable form.

Cyanobenzeneparasulphonic acid.—This acid was prepared by Remsen, Hartmann and Muckenfuss* from the parasulphonamide of benzoic acid. It is more easily prepared from diazobenzenesulphonic anhydride by treatment with cuprous potassium cyanide. The method adopted was as follows: 17 grm. of sulphanilic acid were diazotised by sodium nitrite in the usual way; the diazo-compound was then made into a sludge with water and added slowly to a previously prepared *cold* solution of cuprous cyanide (made by adding gradually a hot solution of 56 grm. of potassium cyanide in 200 c.c. water to a boiling solution of 32 grm. of crystallised copper sulphate in 200 c.c. water). It was found to be important to keep the temperature below 20° while adding the diazo-compound. Finally, the cold mixture was acidified with hydrogen chloride (to decompose the cyanides) until no further precipitate of cuprous cyanide was produced. The solution was boiled to remove hydrogen cyanide and the liquid concentrated after the cuprous cyanide had been filtered off. The solid product was extracted with hot methylated spirit, in which the potassium cyano-sulphonate is soluble. The amount of sulphonate finally obtained as a crystalline, almost colourless salt was about 70 per cent. of the theoretical amount calculated from the diazo-compound.

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* 'Amer. Chem. Journ.,' 1896, p. 150.

Paracyanobenzenesulphochloride, $C_6H_4(CN).SO_2Cl$.—This chloride crystallises readily in measurable form from benzene.

(Found Cl (sulphonic) 17·6 per cent.; N 7 per cent.; $C_6H_4CN.SO_2Cl$ requires Cl (sulphonic) 17·59 per cent.; N 6·93 per cent.)

System: Orthorhombic.

Axial ratios: $a : b : c = 1{\cdot}139 : 1 : 1{\cdot}709$.

Forms observed: {001}, {111}, {110}.

Angle	No. of observations	Limits	Mean	Calculated
001 : 111	35	42° 43′— 43° 29′	43° 5	43° 4′
111 : 110	47	46 36 — 47 20	46 56	—
110 : $\bar{1}11$	23	105 4 —105 35	105 14	—
110 : $1\bar{1}1$	22	74 36 — 74 59	74 46	74 46
110 : $1\bar{1}0$	12	67 4 — 67 43	67 22	67 22
110 : $\bar{1}10$	12	112 13 —112 50	112 38	112 38

Paracyanobenzenesulphonamide, $C_6H_4(CN).SO_2.NH_2$.—This amide crystallises readily in measurable form from acetone; it is easily soluble in hot water.

System: Orthorhombic.

Axial ratios: $a : b : c = 0{\cdot}793 : 1 : 0{\cdot}537$.

Forms observed: {010}, {110}, {011}, {101}.

Angle	No. of observations	Limits	Mean	Calculated
010 : 011	32	51° 18′— 52° 14′	51° 35′	—
011 : 101	16	63 40 — 64 10	63 55	—
011 : 01̄1̄	20	76 26 — 77 2	76 48	76° 50′
011 : 1̄01̄	15	115 45 —116 27	116 9	116 5
101 : 1̄01	7	67 40 — 68 28	68 8	68 16
101 : 101̄	8	111 30 —112 16	111 53	111 44

Crystals of this substance, like those of the other amides measured, gave an electric discharge from opposite ends of an axis.

The magnesium salts of the three acids containing halogen were also prepared in order to compare them with the benzene- and dichlorobenzene-sulphonates considered in Part IV. The structure of these and the corresponding ferrous and cobalt salts is discussed in Part VII.

Well developed crystals of the three salts were obtained in the form of thick prisms by the slow evaporation of aqueous solutions at 25° C. All three salts are closely isomorphous and contain six molecular proportions of water of crystallisation.

$(C_6H_4BrSO_3)_2Mg.6H_2O$:—Water found 18·55 per cent.; calc. 17·88 per cent.
$(C_6H_4ISO_3)_2Mg.6H_2O$:— „ 14·89 „ „ 15·47 „

A determination of Mg in the dehydrated Br-salt gave 4·95 per cent. Mg. The formula $(C_6H_4Br.SO_3)_2$ Mg requires 4·90 per cent. Mg.

Magnesium parachlorobenzenesulphonate, $(C_6H_4Cl.SO_3)_2Mg.6H_2O$.—
System: Monosymmetric.
Axial ratios: $a : b : c = 3{\cdot}6870 : 1 : 0{\cdot}9223$. $\beta = 93° 12'$.
Forms observed: $a\{100\}, r\{101\}, s\{\bar{1}01\}, d\{301\}, m\{110\}, n\{310\}, q\{011\}$.

Angle	No. of observations	Limits	Mean	Calculated
100 : 310	16	50° 40′— 51° 4′	50° 52′	—
310 : 110	2	23 54 — 23 59	23 56	23° 54′
310 : 3̄10	9	77 56 — 78 24	78 13	78 16
101 : 310	11	79 12 — 79 33	79 19	—
310 : 1̄01̄	11	100 29 —100 46	100 40	100 39
100 : 301	8	51 6 — 51 58	51 10	51 21
301 : 101	8	21 12 — 21 41	21 34	—
100 : 101	9	72 32 — 53 10	72 44	72 55
101 : 1̄01	6	27 28 — 28 0	27 41	27 34
101 : 1̄00	6	106 56 —107 24	107 6	107 5
1̄01 : 1̄00	5	79 11 — 79 33	79 25	79 31
101 : 011	1	——	44 0	44 20
011 : 1̄10	1	——	50 30	50 6
1̄10 : 1̄01̄	1	——	85 26	85 34
310 : 1̄10	1	——	54 35	54 32

Magnesium parabromobenzenesulphonate $(C_6H_4Br.SO_3)_2Mg.6H_2O$.—
System: Monosymmetric.
Axial ratios: $a : b : c = 3·7380 : 1 : 0·9094$. $\beta = 93° 51'$.
Forms observed: $a\{100\}$, $r\{101\}$, $s\{\bar{1}01\}$, $m\{110\}$, $n\{310\}$, $q\{011\}$.

Angle	No. of observations	Limits	Mean	Calculated
100 : 310	31	51° 1′— 51° 50′	51° 15′	—
310 : 110	16	23 27 — 23 51	23 41	23° 46′
310 : $\bar{3}10$	9	77 28 — 77 45	77 37	77 30
310 : $\bar{1}10$	11	53 43 — 54 4	53 52	53 44
110 : $\bar{1}10$	3	30 12 — 30 18	30 14	29 58
101 : 310	17	79 7 — 79 30	79 17	—
310 : $\bar{1}0\bar{1}$	16	100 30 —100 49	100 40	100 43
100 : 101	8	72 28 — 73 10	72 46	72 43
101 : $\bar{1}01$	8	107 24 —107 35	107 14	107 17
101 : 011	11	43 49 — 44 10	43 58	—
011 : $\bar{1}10$	9	50 17 — 50 32	50 25	50 24
$\bar{1}10$: $\bar{1}0\bar{1}$	8	85 38 — 85 55	85 45	85 38
$\bar{1}10$: 101	7	94 8 — 94 26	94 19	94 22

Magnesium pariodobenzenesulphonate, $(C_6H_4I.SO_3)_2Mg.6H_2O$.—
System: Monosymmetric.
Axial ratios: $a : b : c = 3·7965 : 1 : 0·9148$. $\beta = 93° 1'$.
Forms observed: $a\{100\}$, $r\{101\}$, $d\{301\}$, $m\{110\}$, $n\{310\}$, $q\{011\}$.

Angle	No. of observations	Limits	Mean	Calculated
100 : 310	17	51° 26′— 51° 50′	51° 41′	—
310 : 110	11	23 26 — 23 36	23 31	23° 34′
310 : $\bar{3}10$	5	76 32 — 76 38	76 36	76 38
310 : $\bar{1}10$	11	52 58 — 53 10	53 2	53 4
110 : $\bar{1}10$	4	29 27 — 29 36	29 30	29 30
100 : 101	5	73 34 — 73 40	73 37	—
100 : 301	3	52 10 — 52 45	52 25	52 10
301 : 101	3	21 15 — 21 28	21 20	21 27
101 : $\bar{1}00$	3	106 16 —106 23	106 20	106 23
301 : 310	10	67 27 — 67 46	67 39	—
310 : $01\bar{1}$	10	52 18 — 52 45	52 29	52 42
$01\bar{1}$: $\bar{3}0\bar{1}$	10	59 43 — 59 56	59 50	59 39